

POLY-*O*-AMINOPHENOL OBTAINED AT HIGH POTENTIALS BY CYCLIC VOLTAMMETRY ON SnO_2 :F ELECTRODES. APPLICATION IN QUANTITATIVE DETERMINATION OF ASCORBIC ACID

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ABSTRACT

In the present work the obtention of poly-*o*-aminophenol (POAP) at high potentials on conducting glass (SnO_2 :F) is reported. The synthesis was carried out by continuous potential cycling in a 1×10^{-3} M *o*-aminophenol (OAP), 0.1 M hydrochloric acid, and 0.1 M potassium chloride solution between -0.2 and 1.5 V at $0.05 \text{ V}\cdot\text{s}^{-1}$ vs Ag|AgCl. The polymer growth was followed by cyclic voltammetry, UV-vis spectra, and AFM characterization. The SnO_2 :F modified electrode (SnO_2 :F/POAP) was tested in the electro-oxidation of ascorbic acid (AA) in phosphate buffer solution. This coating showed an important electrocatalytic effect because a negative anodic shift of 0.4 V with respect to a bare SnO_2 :F glass electrode was observed.

Keywords: Fluor-doped Tin oxide, *o*-aminophenol, Electropolymerization, Ascorbic acid, Electrocatalysis, Modified electrode.

INTRODUCTION

Although polymeric materials have been deposited onto substrates using a variety of approaches, *e.g.*, covalent bond, adsorption, physical mixture, etc., it seems that electropolymerization is the most convenient way because the method represents a simple, neat, and efficient route to polymers synthesis. The use of electrochemical techniques enables the rate and extension of the process to be carefully controlled by applying appropriate electrochemical conditions. Furthermore, physical and chemical properties of the obtained polymer are also controlled during the synthetic process by the same electrochemical conditions. One of such conditions is the substrate selected for the obtention of a conductive polymer. Among the commonest substrates utilized for this purpose are glassy carbon¹⁻⁹, platinum^{2, 4, 5, 7, 8, 10-17}, gold^{4, 7, 18-27}, carbon paste^{28, 29}, transparent indium tin oxide^{18, 19, 30}, Cu¹⁸, Ag³¹, SnO_2 ³², etc. However, it is always advisable to employ other electrodic substrates for the fabrication of modified electrodes.

Tin oxide is a metallic semiconductor which is a good choice for the elaboration of modified electrodes, since it has demonstrated to have important applications in microelectronic and photoelectronic devices, photovoltaic cell, and gas-sensing materials³³⁻³⁵. In addition, it is a low cost material, has high chemical stability, and possesses electrical properties that make it an appropriate industrial material. However, application of this material to elaborate novel electrodes to be utilized in the electrochemical field³⁵⁻³⁹ is still necessary. In this respect fluorine-doped tin oxide (SnO_2 :F) has been employed for the obtention of poly(tetraaminophenyl)porphyrins modified electrodes that have been used in aqueous electro-catalytic applications for hydrazine⁴⁰, nitrite⁴¹, and nitrate⁴². Consequently, among the many available substrates usually employed for the electro-synthesis of conductive polymers (see above ref.), commercial and home-prepared fluorine-doped tin oxide, was selected. This compound allows the use of a wide potential range in aqueous medium^{35, 43}. In neutral and acid medium this range goes up to *ca.* 1.8 V vs Ag|AgCl. At this highly anodic potential, oxidative degradation of the polymeric film and its irreversible spoilage occurs^{44, 45}.

On the other hand, the electrochemical oxidation of *o*-aminophenol produces electroactive dimers which polymerize to form an electroactive material on the electrode surface, POAP^{2, 8, 17}. POAP has been characterized^{4, 7-9, 25, 30}, its electrochemical and electrochromic properties studied^{6, 16, 23, 46} and the material applied to sensors^{28, 29, 47, 48}. One of these applications is, for example, as a typical nonconducting film and effective barrier to protect the electrode from fouling. POAP films have been successfully employed in the development of hydrogen peroxide, glucose, and uric acid biosensors^{10, 20, 29, 49, 50}.

Recently, OAP has been utilized as monolayer⁵¹ and as aniline copolymer³ on glassy carbon electrode. Both modified electrodes displayed electrocatalytic effect for ascorbic acid (AA) oxidation. Nevertheless no references have been found in the literature concerning to the use of Poly-OAP in the electrochemical oxidation of AA.

In the present work the electropolymerization at high positive potentials of *o*-aminophenol (OAP) on fluor-doped tin oxide (conducting glass electrode) is proposed. An electrode modified in this way is promising because the material may present electrocatalytic and analytical applications and consequently our first step was the assessment of the device in the electro-oxidation of ascorbic acid.

EXPERIMENTAL

Materials

All chemicals used in this work were of analytical grade and used without further purification. *o*-aminophenol (OAP) was obtained from ICN Pharmaceuticals Inc., USA. The supporting electrolytes used for electrochemical experiments were 0.1 M HCl + 0.1 M KCl solution, or phosphate pH 7.4 buffer solutions (PBS), prepared from 0.1 M NaCl, 0.0026 M KCl, 0.04 M Na_2HPO_4 and 0.01 M KH_2PO_4 . Ascorbic acid (AA) and other reagents were purchased from Merck, Germany. All aqueous solutions were prepared with doubly distilled deionized water. Prior to each experiment the solution was deoxygenated by flushing with argon (99.99 %) for 20 min. All experiments were conducted at room temperature (20 °C), under argon atmosphere.

Apparatus

Electrochemical measurements were performed on a CHI Instruments potentiostat Model 900B using a conventional three-electrode cell. A fluor-doped tin oxide conducting glass and platinum wire were used as working and counter electrode, respectively. All cell potentials in this work were measured with respect to an Ag|AgCl, KCl (sat'd) reference electrode (0.197 V vs NHE). UV-vis absorption spectra were registered on a Specord 40 Spectrophotometer (Analytik Jena). All recorded spectra were baseline corrected. Morphology studies of the working electrode surface were performed *ex situ* on a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) using tapping-mode AFM. A silicon tip (Olympus) with a resonance frequency of 300 kHz was used.

Electrodes

SnO_2 :F electrodes were manufactured by coating a layer of tin oxide on a glass substrate (0.9 cm²). SnO_2 :F substrates were supplied by SOLEMS, France. Prior to use, the working electrode was cleaned using the H_2O_2 procedure described by Osada et al.⁵². The substrate was treated with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ (30%)/ NH_4OH (25%) solution (5:1:1 vol) at 80°C for 20 min, followed by rinsing with boiling distilled H_2O for 5 min. The use of boiling water has proven to be useful to obtain impurity-free surfaces.

Procedure

Electropolymerization was conducted by successive potential cycling at $0.05 \text{ V}\cdot\text{s}^{-1}$ between -0.2 and 1.5 V, in a 0.1 M HCl + 0.1 M KCl solution containing $1 \cdot 10^{-3}$ M *o*-aminophenol (OAP). After polymerization, the modified electrode was thoroughly washed with water. Then the electropolymerized film was stabilized in a PBS solution by successive potential cycling between the potential limits at which AA oxidation studies are performed.

RESULTS AND DISCUSSION

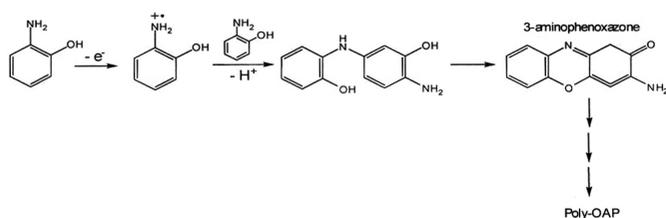
Electrochemical polymerization of OAP

Figure 1 shows cyclic voltammograms registered during the electropolymerization of OAP on a SnO_2 :F conducting glass electrode into a $1 \cdot 10^{-3}$ M OAP, 0.1 M HCl, and 0.1 M KCl working solution obtained by cycling between -0.2 and 1.5 V vs Ag|AgCl at $0.05 \text{ V}\cdot\text{s}^{-1}$ (35 cycles). As it can be seen in the first cycle, there is only one anodic process, starting at 0.6 V and assigned to the oxidation of the hydroxyl group of OAP⁵³, and the current continuously increases, owing to the oxidation of the amine group, that finally

leads to OAP polymerization⁵⁴. Reported works indicate that the obtained films showed a voltammetric response that depends on the potential applied during the electro-polymerization². Gonçalves *et al.* obtained less electroactive films cycling up to 1.547 V (*vs* Ag|AgCl) on Pt. They also found that when cycling up to 1.397 V *vs* Ag|AgCl on a glassy carbon electrode the response is well defined, regardless of the utilized potential range. This result has been ascribed to an activation process of the glassy carbon electrode rather than to an electroactive film deposited onto the substrate². Usually the most commonly used potential for the obtention of POAP, irrespective of the substrate, is in the -0.2 to 0.9 V (*vs* SCE) range^{3-5, 7, 9, 11, 12, 21-26, 30, 32}.

After the first cycle, two anodic peaks appear at 0.2 V (I_a) and 0.4 V (II_a) due to the formation of a cyclic dimer of OAP, 3-aminophenoxazine (3APZ), and, after continuous potential scanning, the current response of this pair of redox peaks gradually increases. Concomitantly, a new pair of cathodic redox peaks appears at 0.1 V (I_c) and 0.2 V (II_c), respectively. These two pair of peaks are due to the oxidation and reduction of POAP, pointing to the formation of polymeric species (Scheme 1).

F. Armijo *et al*



Scheme 1: Proposed mechanism for the polymerization of *o*-aminophenol.

Thus, during the whole polymerization process, OAP is firstly oxidized to form its cyclic dimer and then the dimer behaves as a new monomer in the following polymerization steps^{46, 3}. The inset in Fig. 1 shows the I (μA) *vs* t (s) relationship corresponding to the voltammetric profiles in Fig. 1. In this case, an increase in charge was observed at the onset of the polymerization but at the end of it the charge exhibits a very large drop ascribed to a low conductivity film formation. Electropolymerization affords a brown film on the electrode surface.

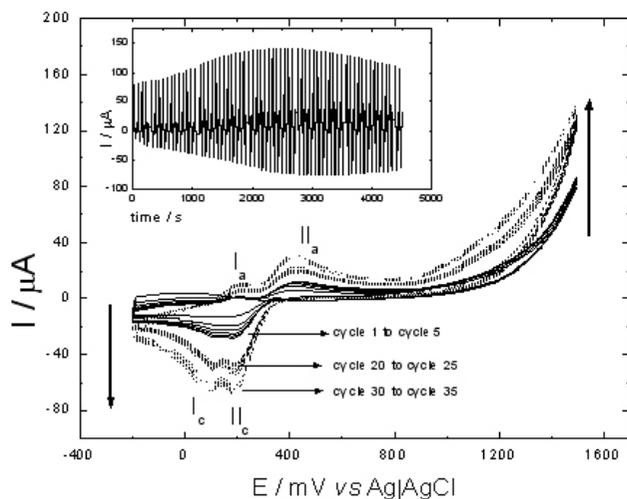


Fig. 1.- Voltammetric response during the electropolymerization of *o*-aminophenol on SnO_2 :F glass electrode from a solution containing *ca.* 0.1 mM OAP + 0.1 M HCl + 0.1 M KCl between -0.2 and +1.5 V at 0.05 $\text{V}\cdot\text{s}^{-1}$. Inset is current, I , versus time, corresponding to the voltammetric profiles of Fig. 1.

Characterization of POAP film electrodes

UV-vis spectrum

The OAP monomer is unstable in aqueous acid media, which is evidenced by the brownish color the solution takes after successive potential cycling

during the electropolymerization process. Each deconvoluted spectrum led to three or four main absorption bands, depending on the time at which the measurement was made. Gonçalves *et al.*² have reported similar results for UV-vis spectra taken *in situ* for the electrolysis of an OAP aqueous solution. In the present work, well defined bands at 397 nm, 464 nm, 535 nm and 735 nm, in a 0.1 M HCl + 0.1 M KCl solution containing $1\cdot 10^{-3}$ M OAP (not shown), were obtained.

Figure 2 depicts the UV-vis spectrum of the electrode obtained from open circuit potential using different electropolymerization steps (number of cycles) ranging from 25 to 80 cycles. Four absorption peaks located at 410 nm (I), 472 nm (II), 567 nm (III), and 700 nm (IV) are observed. Bands II and IV have been reported for potentiodynamically synthesized POAP⁵⁵, but recently Shah and Holze obtained the same absorption bands for POAP films prepared on ITO coated glass at 0.8 V²⁴. The absorption band II corresponds to the cation radical of OAP⁴⁶. Band I arises at very early stages of electropolymerization. This peak is characteristic of the oxidized form of POAP^{30, 19, 56}. The intensity of both bands increases during continuous electro-oxidation, which has been ascribed to a two-step electro-oxidation mechanism. By applying a suitable anodic potential, electro-oxidation of OAP proceeds giving rise to a reaction intermediate that absorbs at 460 – 470 nm. In the following chemical step, the intermediate reacts with solution phase OAP yielding oligomers or polymers as product of this successive process. Absorbance of the electropolymerized final product was 410 nm⁵⁷.

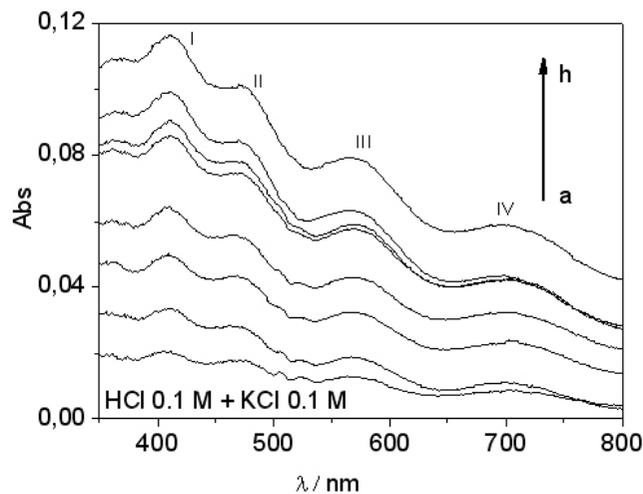


Fig. 2.- UV-Vis spectra at open circuit potential of a POAP-coated SnO_2 :F glass electrode, obtained at different number of cycles: (a) 25, (b) 35, (c) 40, (d) 50, (e) 60, (f) 65, (g) 75, and (h) 80.

Intensity of the absorption band at 567 nm (III) increases during continuous electro-oxidation. Ohsaka *et al.* observed this band at 600 nm in the reduced state of a potentiodynamically prepared POAP film⁵⁸. However, no absorption band was observed at 750 nm as reported elsewhere for the potentiodynamically prepared POAP film⁵⁵. To confirm the presence of an absorption band at 750 nm Shah and Holze potentiodynamically deposited POAP on ITO glass by cycling the potential between -0.2 V and 0.84 V *vs* SCE¹⁹. The results agree with those reported by Ohsaka *et al.*⁵⁸. The UV-vis spectrum of the electrode obtained in this work indicates that the obtained polymer presents multiples redox states. Moreover, this spectrum is due to the presence of oligomeric fragments in the film with different conjugation length.

Finally, the UV-vis spectrum indicates that a polymeric film of POAP is formed on the electrode and this film is mainly composed by phenoxazine units^{2, 7}.

AFM Characterization

Figure 3 A-C shows typical high resolution AFM images corresponding to a bare SnO_2 :F electrode (Fig. 3A) and after OAP electropolymerization on SnO_2 :F conducting glass substrate by CV, 50 cycles (Fig. 3B) and 100 cycles (Fig. 3C), respectively. Figure 3A shows the typical amorphous morphology of SnO_2 :F surface with a RMS roughness of 47.35 nm. Figures 3B and 3C show the formation of a homogeneous granular film on SnO_2 :F electrode surface after 50 and 100 cycles, respectively. The roughness of the surface decreases to

32.54 nm and 33.5 nm, respectively, this diminution could be attributed to the filling of the interparticle spaces of SnO₂: F by the POAP particles. The particle size was 187 nm and 283 nm for the POAP of 50 and 100 cycles, and the increase in the particle size is due to the growth of the polymer with the major number of cycles. In addition, it is noteworthy that although the morphology reported by other authors is scarce, the morphology observed here agrees well with that reported by SEM^{30,22}.

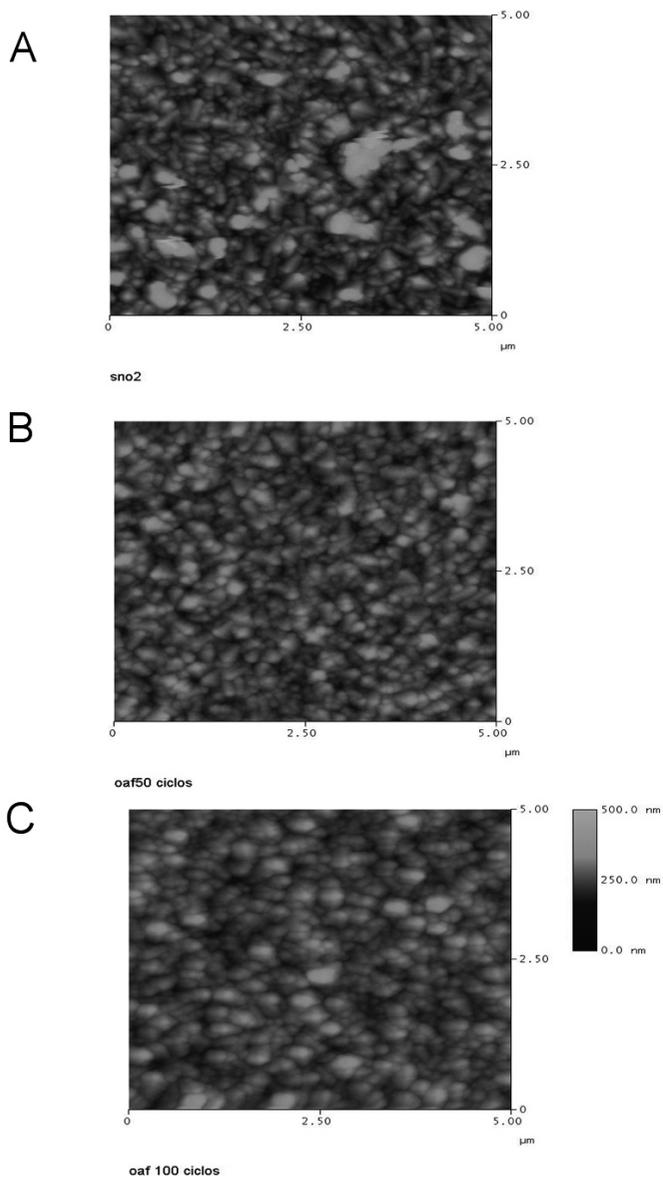


Fig. 3.- AFM images corresponding to bare SnO₂: F electrode (A) and after cyclic voltammetric electropolymerization of the OAP on SnO₂: F conducting glass substrate, 50 cycles (B) and 100 cycles (C).

Electrocatalytic oxidation of ascorbic acid (AA).

As for the practical applications of this polymer, the membrane properties displayed by POAP have been successfully exploited^{11,28,29,59} and the possibility of using POAP as sensor for cations has been studied^{14,60}. However, either in practical use or in active investigation concerning the thermodynamic and kinetic properties of POAP the polymer redox process and its dependence from the external solution pH plays an important role because at pH's greater than 4 the polymer becomes nonelectroactive^{5,21,24}.

Consequently, the effect of some experimental parameters on the electrochemical characteristics of the resulting films were investigated and optimized according to ascorbic acid oxidation response.

Electrochemical oxidation of AA at poly-OAP by Cyclic voltammetry

Figure 4 depicts the voltammetric profile of the stabilization of SnO₂: F/ POAP obtained by continuous potential cycling between -0.8 and 1.4 V at 0.1 Vs⁻¹ in PBS buffer solution, pH: 7.4. The POAP used in the electrocatalytic studies was that obtained by 40 potential cycles because this electrode displayed the highest electrocatalytic effect. The electrodes obtained by larger number of potential cycles showed a lower effect probably due to the low conductivity of the polymeric film. Besides, the film thickness effect upon the permeability of the electroactive species has been attributed to morphological changes of the polymer as the film thickness varies²².

In Fig. 4, two anodic, -0.19 V and 0.92 V, and two cathodic, -0.31 V and 0.60 V, peaks appear during the first cycle. These peaks disappear during the stabilization of the polymer in neutral medium and only a capacitive response is observed after 30 cycles. Nevertheless, the voltammetric response is recovered when the modified electrode is returned to an acid media. The effect of the acid concentration of the solution wherein the electrode is stabilized on the electronic transport was ascribed to a different protonation degree of redox centers of the polymer, which affect the electron hopping process. Permeation of the electroactive species across the polymer decreases as the acid concentration in solution decreases, which would influence the polymer swelling²². This behavior could be attributed to deprotonation that might occur simultaneously with the intake of anions and agrees with the results obtained by Tucceri and Zhang *et al.*^{24,61}. The imine groups of oxidized POAP were unprotonated and the degree of protonation decreases as pH increases. The inset in Fig. 4 depicts the voltammetric profile between -0.8 V and 1.4 V at 0.1 V·s⁻¹ of SnO₂: F/POAP and bare SnO₂: F. The modified electrode shows a capacitive response and reduction current wave is observed around -0.35 V, probably due to the response of the substrate electrode. Different workers have described that POAP exhibited its maximum electroactivity in the potential range -0.2 < E < 0.5 V (vs SCE) at pH lower than 3^{5,16,55}. They have also reported that POAP conductive potential range was found at potentials more negative than the formal potential, defined as (E_{pc} + E_{pa}) / 2, of the polymer¹⁶. Moreover, a pH effect exists: as pH increases from acidic to neutral the film becomes nonelectroactive. Thus, if stabilization of SnO₂: F/POAP in a PBS buffer solution, pH 7.4, in the range potential - 0.8 to 1.4 V vs Ag|AgCl, is accomplished, an electrode modified with an electrochemically nonactive polymer in neutral solution should be obtained. Nevertheless, when oxidation tests with electroactive solutes, such as AA, were performed, electrocatalytic activity was observed.

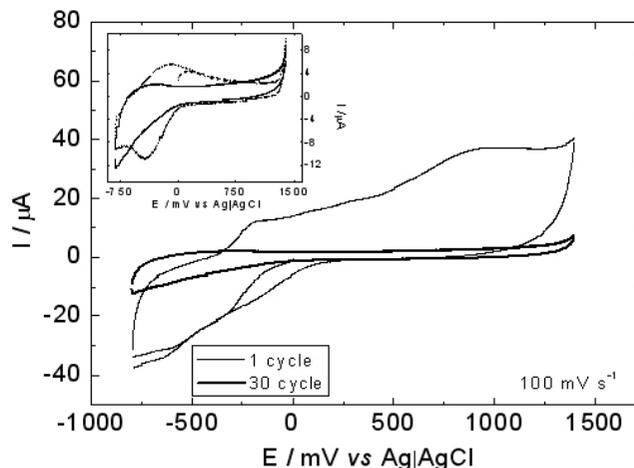


Fig. 4.- Voltammetric profile of the stabilization of SnO₂: F/POAP (40 potentiodynamic cycles) performed by continuous potential cycling, 1 cycle (thick line) and 30 cycle (full line), respectively. Inset depicts the voltammetric response of the SnO₂: F/POAP (full line) and bare SnO₂: F glass electrode (thick line), in PBS buffer solution, between -0.8 V and 1.4 V at 0.1 V·s⁻¹.

Figure 5 shows the cyclic voltammograms of 1·10⁻³ M AA on SnO₂: F/ POAP at different scan rates. The shift towards higher values of the catalytic oxidation peak potential with increasing sweep rates can be observed, indicating a kinetic limitation in the reaction between redox sites of SnO₂: F/POAP film and AA. However, the cyclic voltammetric peak currents for AA at SnO₂: F/ POAP are linearly related to the square root of scan rate in the range 5 - 40

$\text{mV}\cdot\text{s}^{-1}$ (bottom in Fig. 5), *i.e.*, the process is diffusion controlled. The inset in Fig. 5 shows cyclic voltammograms recorded at $5 \text{ mV}\cdot\text{s}^{-1}$ of $1\cdot 10^{-3} \text{ M}$ AA on (a) SnO_2 : F/POAP; and (b) SnO_2 : F, respectively. As can be seen here the oxidation peak of AA at about 1.2 V is broad on SnO_2 : F. On the other hand, even though the peak current is lower the peak potential shifts negatively to 0.78 V on SnO_2 : F/POAP, this fact corroborates that the substrate is completely covered by the polymer film. The oxidation shift towards lower potentials for the electro-oxidation of AA demonstrate the electrocatalytic effect of SnO_2 : F/POAP on AA. The overpotential shift is due to a kinetic effect, thus a substantial increase in the rate of electron transfer is observed for AA indicating an improvement in the reversibility of the electron-transfer process when compared to bare SnO_2 : F.

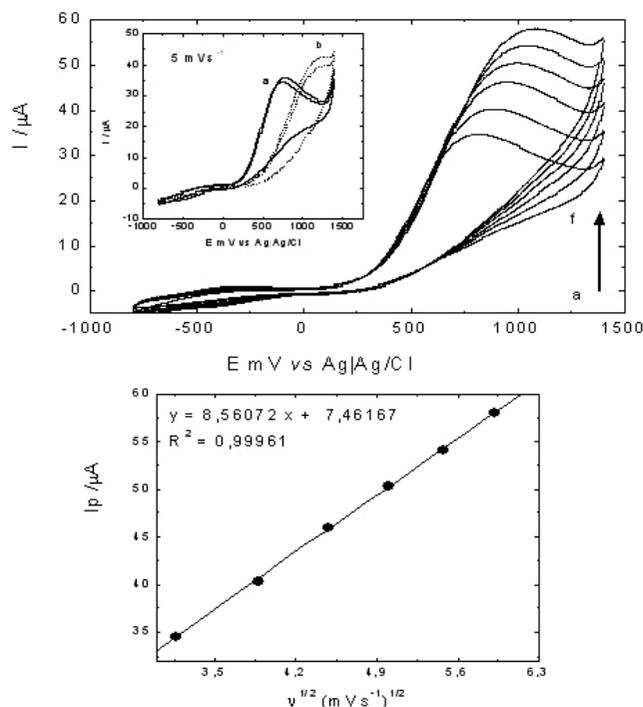


Fig. 5.- Voltammetric response of $1\cdot 10^{-3} \text{ M}$ AA solution on SnO_2 : F/POAP in PBS (pH= 7.4) at different scan rates: (a) 0.01, (b) 0.015, (c) 0.02, (d) 0.025, (e) 0.03 and (f) $0.035 \text{ V}\cdot\text{s}^{-1}$. Inset shows the voltammetric response of $1\cdot 10^{-3} \text{ M}$ AA solution on (a) SnO_2 : F/POAP, and (b) bare SnO_2 : F glass electrode in PBS (pH= 7) at $0.005 \text{ V}\cdot\text{s}^{-1}$. Bottom figure shows $I \times v^{-1/2}$ line.

Figure 6 shows cyclic voltammograms for different concentrations of AA on SnO_2 : F/POAP. Increase of the oxidation peak current with increasing AA concentration is observed. The inset to Fig. 6 shows a linear relationship between anodic peak current and AA concentration in the range $4\cdot 10^{-4} - 1.4\cdot 10^{-3} \text{ M}$, with a correlation coefficient of 0.9966.

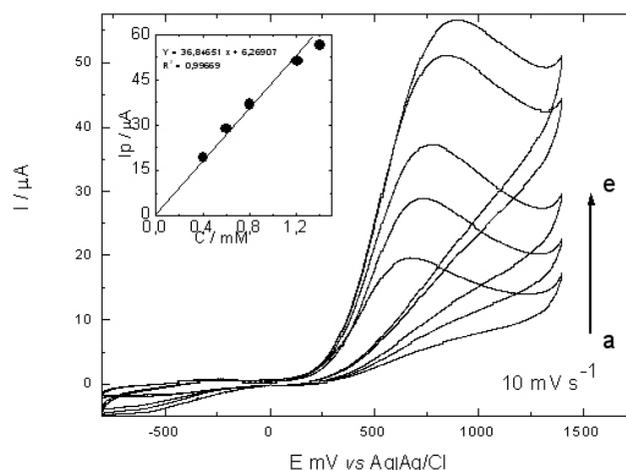


Fig. 6.- Voltammetric response at different concentrations of AA on SnO_2 : F/POAP in PBS (pH= 7.4) at $0.010 \text{ V}\cdot\text{s}^{-1}$. Concentrations of AA from (a) to (e) are $4\cdot 10^{-4}$, $6\cdot 10^{-4}$ M, $8\cdot 10^{-4}$ M, $1.2\cdot 10^{-3}$ M, $1.4\cdot 10^{-3}$ M, respectively. Inset: electrocatalytic peak current (from CVs of Fig. 6) vs AA concentration.

To verify the reproducibility of SnO_2 : F/POAP, successive measurements of a $1\cdot 10^{-3} \text{ M}$ AA solution were made. The results of 10 consecutive measurements showed a relative standard deviation of 5.2 % for AA, proving that the modified electrode is not subject to surface fouling by the oxidation products.

CONCLUSIONS

The electrochemical preparation of poly-*o*-aminophenol at high potentials has been obtained from a $1\cdot 10^{-3} \text{ M}$ OAP, 0.1 M hydrochloric acid and 0.1 M potassium chloride solution in the potential range between -0.2 and 1.5 V at $0.05 \text{ V}\cdot\text{s}^{-1}$ on a SnO_2 : F conducting glass electrode. The SnO_2 : F/POAP obtained by 40 cycles has good electro-activity in neutral medium. At pH 7.4 PBS, SnO_2 : F/POAP exhibits good electrochemical activity for the oxidation of AA. The kinetic process of the catalytic reaction can be studied by cyclic voltammetry. The modified electrode prepared is very stable and can be utilized for the quantitative determination of AA.

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